

Appendix 4A-4: Annual Permit Compliance Monitoring Report for Mercury in Stormwater Treatment Areas

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KEY FINDINGS AND OVERALL ASSESSMENT

This report summarizes data from compliance monitoring of mercury storage, release, and bioaccumulation in stormwater treatment areas (STAs) during the reporting year May 1, 2001 through April 30, 2002. Results from this monitoring program describe significant spatial distributions and, in some instances, between-year differences in mercury concentrations.

Key findings are as follows:

1. During the monitoring period, there were no violations of the Florida Class III numerical Water Quality Standard (WQS) of 12 ng total mercury (THg)/L. As such, the project has met the requirements of Section 6.i of the mercury monitoring program of the referenced permits.
2. STA-1W, which subsumed the Everglades Nutrient Removal (ENR) Project in early 2000, continued to have only low concentrations of methylmercury (MeHg) in surface water, consistently showed negative percent change across the STA, and exhibited greatly reduced MeHg bioaccumulation in resident fish relative to other STAs and other Everglades areas.
3. After four years of operation, STA-6 continued to exhibit fluctuations in Hg species in water and Hg levels in resident fish. Following a drydown and rewetting event during the second quarter of 2001, concentrations of THg and MeHg in the unfiltered surface water spiked at STA-6 outflows, reaching 7.0 ng THg /L and 3.4 ng MeHg/L. While a scoping level assessment found THg loads out of STA-6 to be similar to or less than inflow loads (including atmospheric deposition), loads of MeHg out of the STA were found to exceed inflow loads by 2 to 7 grams. A more intensive followup study is planned to more accurately quantify annual average MeHg export. Resident fishes continued to exhibit a positive percent change in Hg across STA-6; however, there was no evidence that the spike in water column MeHg was followed by significant increases in mercury bioaccumulation over background. While levels of Hg in STA-6 fishes have fluctuated near background and are similar to or lower than levels found in other Everglades areas, fish-eating wildlife feeding preferentially at STA-6 face some risk of adverse chronic effects from mercury exposure based on United States Fish and Wildlife Service (USFWS) and United States Environmental Protection Agency (USEPA) criteria.
4. Concentrations of THg and MeHg in sediment cores collected from STA-5 in 2001 remained at background levels observed in cores collected in 1998, and continued to be within the

expected range for Everglades soils. During the reporting year, THg and MeHg concentrations in surface water generally exhibited a negative percent change across STA-5. Further, levels of Hg in mosquitofish from the interior marshes of STA-5 declined from peak levels observed during the second semi-annual collection in 2000, and contained roughly 50 percent less Hg than fish from either the inflows or outflows. Levels of Hg were generally similar in mosquitofish at inflow and outflows of STA-5. Alternatively, concerns were raised by the observation that Hg concentrations were greater in sunfish from the discharge canal and the interior compared to sunfish from the supply canal. Further, while concentrations of Hg declined over the last three years in sunfish inhabiting the supply canal, levels increased in fish from the interior and the discharge canal in 2000 and remained elevated in 2001 relative to 1999. There is also some evidence to suggest that levels of Hg have increased slightly in largemouth bass in the discharge canal during the monitoring period. Finally, while temporal trends cannot be evaluated for bass inhabiting the interior marshes of STA-5 (due to age distribution of collected fishes), the expected mean concentration of Hg in three-year-old interior bass reached 801 ± 147 ng/g in 2001, which exceeds the state's limited-consumption advisory for human health of 500 ng/g wet weight muscle (0.5 mg/Kg or 0.5 ppm).

INTRODUCTION

This is the fifth annual permit compliance monitoring report for mercury in stormwater treatment areas (STAs). This report summarizes the mercury-related reporting requirements of the U.S. Army Corps of Engineers (USACE) Section 404 Dredge and Fill permit (permit No. 199404532), the Florida Department of Environmental Protection (FDEP) National Pollution Discharge Elimination System (NPDES) permit (FL0177962-001), and FDEP Everglades Forever Act permits (EFA- Ch. 373.4592, F.S.). The latter includes permits for STA-6, STA-5, STA-1W, and STA-2 (No. 06,502590709, 262918309, 0131842, FL0177962-001, 0126704). This report summarizes the results of monitoring in the water year ending April 30, 2002. The results of mercury monitoring at sites downstream of the STAs (non-Everglades Construction Project [non-ECP] discharge structures and marshes) will be reported separately in **Appendix 2B-3**.

This report consists of key findings and an overall assessment, an introduction and background, a summary of the Mercury Monitoring and Reporting Program, and monitoring results. The background section briefly summarizes the operation of the STAs and discusses their possible impact on South Florida's mercury problem. The section also includes site descriptions and maps of each STA currently being monitored (in the order they became operational). The following section summarizes both sampling and reporting requirements of the Mercury Monitoring Program within the STAs. Monitoring results are summarized and discussed in two subsections: (1) results from pre-operational monitoring, and (2) results from STA operational monitoring. Recent results from the Mercury Monitoring Program describe significant spatial distributions and, in some instances, between-year differences in mercury concentrations.

BACKGROUND

The STAs are treatment marshes designed to remove nutrients from stormwater runoff originating from upstream agricultural areas and Lake Okeechobee releases. The STAs are being built as part of the Everglades Construction Project (ECP). When completed, the ECP will include seven STAs totaling about 50,000 acres of constructed wetlands. The downstream receiving waters to be restored and protected by the ECP include the South Florida Water Management District's (SFWMD's or District's) water management canals of the Central and

Southern Florida (C&SF) Project and the interior marshes of the Everglade's Protection Area, encompassing Water Conservation Areas (WCAs) 1, 2, and 3, and Everglades National Park (ENP or Park).

The problem form of mercury in aquatic ecosystems is an organic form called methylmercury, which is produced by natural bacteria living in sediments from the inorganic form of mercury in storm runoff, rain, and peat soils under conditions devoid of dissolved oxygen. Methylmercury is a persistent, bioaccumulative, toxic pollutant that can build up in the food chain to levels harmful to humans, fish-eating wildlife and their predators. Widespread, elevated concentrations of mercury were first discovered in freshwater fish from the Florida Everglades in 1989 (Ware et al., 1990). In the Arthur R. Marshall Loxahatchee National Wildlife Refuge (Refuge) and the Big Cypress National Preserve, the average concentration in age class 3-year largemouth bass flesh exceeded the state's advisory threshold of 0.5 parts per million (ppm) for limited fish consumption, but were less than the state's no-consumption advisory threshold of 1.5 ppm; the remainder of the Everglades exceeded the no-consumption threshold. Consequently, in March 1989 state fish consumption advisories were issued for select species and locations (Florida Department of Health and Rehabilitative Services and Florida Game and Fresh Water Fish Commission, March 6, 1989). Subsequently, elevated concentrations of mercury were also found in predators such as raccoons, alligators, Florida panthers, and wading birds (see Fink et al., 1999).

To provide assurance that the ECP is not exacerbating the mercury problem, the District monitors concentrations of mercury (THg) and methylmercury (MeHg) in various abiotic (e.g., water and sediment) and biotic (e.g., fish and bird tissues) media. Monitoring mercury concentrations in aquatic animals provides several advantages. First, MeHg occurs at much greater concentration in biota relative to surrounding water, making chemical analysis more accurate and precise. Although detection levels of parts per trillion (ppt or ng/L) have been achieved for THg and MeHg in water, uncertainty boundaries can become large when ambient concentrations are very low, as is often the case in the Everglades. Second, organisms integrate exposure to methylmercury over space and time. While surface water concentrations can fluctuate daily, per event, and seasonally, mosquitofish are a short-lived species that can be used to monitor short-term changes in environmental concentrations of mercury through time. Sunfish and largemouth bass, on the other hand, are long-lived species and represent average conditions that occurred over previous years. Finally, the mercury concentration in aquatic biota is a true measure of MeHg bioavailability and results in a better indication of possible mercury exposure to fish-eating wildlife than the concentration of methylmercury in water.

SITE DESCRIPTIONS

STA-6

STA-6, section 1 is located at the southeastern corner of Hendry County and the southwest corner of the Everglades Agricultural Area (EAA). STA-6, section 1 has two treatment cells (cell 5, with an area of 252 ha, and cell 3, with an area of 99 ha) that are designed to provide a total effective treatment area of 352 ha (870 acres) (**Figure 1**). For additional details see SFWMD, 1997a). The United States Sugar Corporation (USSC) has operated the two cells as a stormwater retention area since 1989. Approximately 4,210 ha of USSC's agricultural production area (Southern Division Ranch, Unit 2) drains into STA-6, section 1 via a supply canal and an existing pump station, G-600, that continues to be under USSC operation. Water flows from the supply canal to the treatment cells via supply canal weirs (two for cell 5 and one for cell 3). Water then

flows in an easterly direction and is discharged through six recently installed culverts (G-354 A, B, and C for cell 5; G-393 A, B, and C for cell 3), each with a fixed-crest weir at 13.6 ft NGVD to limit drawdown of each treatment cell to the desired static water level of 13.6 ft NGVD (maximum combined discharge of 500 cfs). This outfall then enters the discharge canal, which gravity discharges to the L-4 borrow canal via six culverts, which are confluent to G-607. The L-4 borrow canal conveys flows eastward to the S-8 pump station, which discharges into Water Conservation Area 3-A. On demand, water can be conveyed from the L-4 canal backward (using stop logs at G-604 to bypass flows to the L-4 from the G-607 culverts) to the USSC unit 2 farm for irrigation. As a consequence, unlike other STAs, timing, quantity, duration of inflows and backflows, and, thus, mean depth, hydraulic loading rate, and hydraulic residence time (HDT) of STA-6 are controlled by USSC via the operation of G-600.

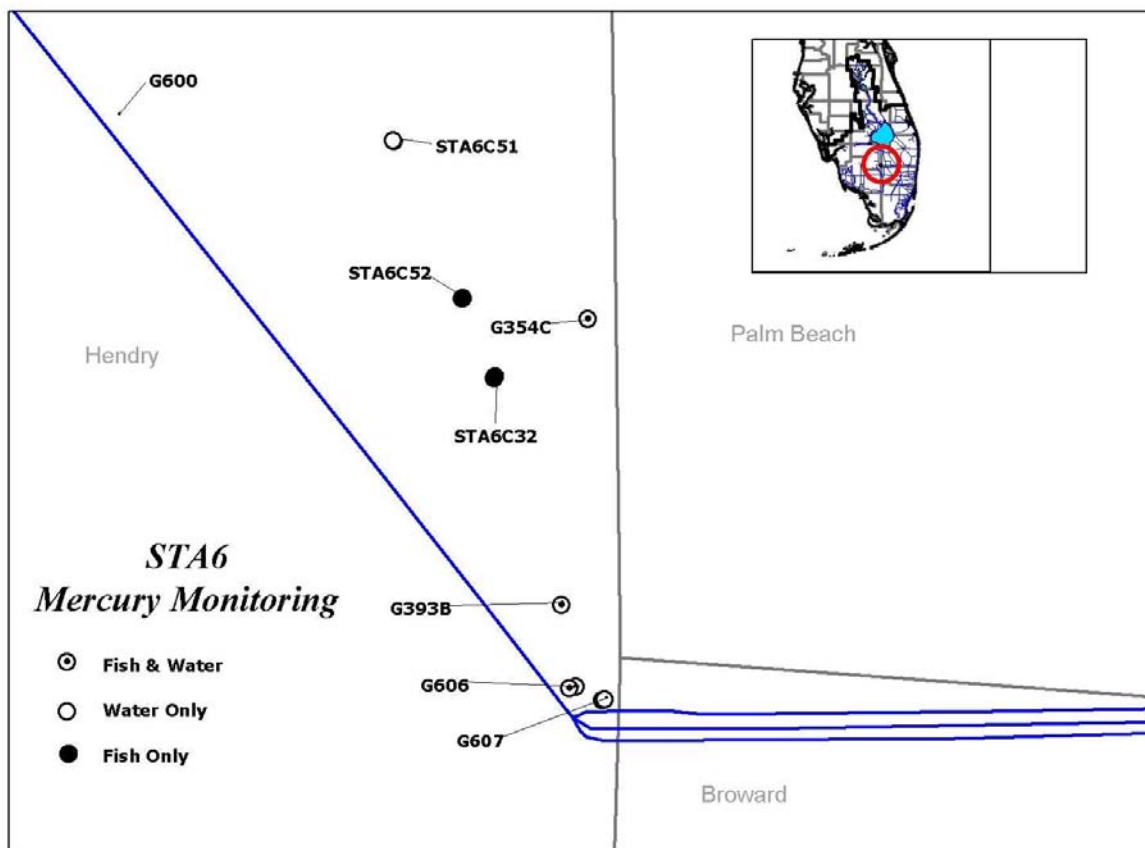


Figure 1. STA-6 mercury monitoring sites

STA-5

STA-5 is immediately north of USSC's Southern Division Ranch, Unit 2 and extends from the L-3 levee on the west to the Rotenberger Tract on the east. STA-5 consists of two parallel treatment cells (cell 1 and cell 2) to provide a total effective treatment area of 1,666 ha (4,118 acres, **Figure 2**; for additional details see SFWMD, 1998a). Under typical operations, water from the L-3 Borrow canal, the Deer Fence canal and the S&M canal gravity-flows into the two treatment cells through four gated supply canal culverts (G-342A, G-342B, G-342C, and G-342D). Water then continues to gravity-flow east through the western portions of the treatment area through eight open culverts into the eastern treatment areas; each treatment cell is subdivided by an internal levee because of a significant downward slope in ground elevation from west to east. Water then gravity flows through four discharge structures (G-344A and B for treatment cell 1, and G-344C and D for treatment cell 2) and then discharge into the STA-5 discharge canal. The STA-5 discharge canal continues along the western and northern sides of the Rotenberger Wildlife Management Area, ultimately emptying into the Miami Canal. However, direct discharge to the Rotenberger Tract is possible and is used to supplement the natural accumulation of water via rainwater on an as-needed basis.

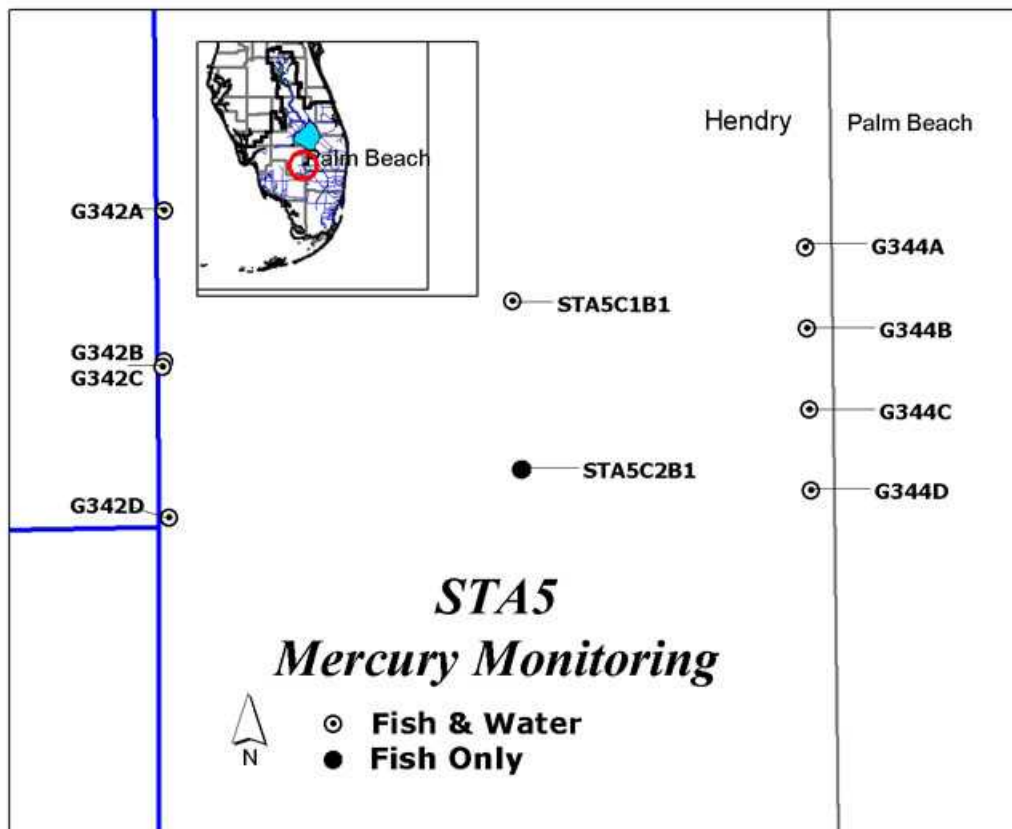


Figure 2. STA-5 monitoring sites

STA-1 WEST

STA-1 West is located in western Palm Beach County, northwest of the Arthur R. Marshall Loxahatchee National Wildlife Refuge (Refuge or WCA-1). STA-1W is designed to provide a total effective treatment area of 6,870 acres, including the 3,815 acres of the existing Everglades Nutrient Removal (ENR) Project (treatment cells 1 through 4), which it subsumed in April 1999 (**Figure 3**) (For additional details see SFWMD, 1998b). Under typical operations, S-5A basin runoff is conveyed to STA-1W from pump station S-5A via STA supply canal and distribution works gated weir structure G-302. Flows will travel in a southwesterly direction via the supply canal into treatment cell 5 via culverts G-304 A through J, and into treatment cells 1 through 4 (existing ENR Project) via gated weir structure G-303. Flows through cell 5 are conveyed in a westerly direction through structures G-305 A through V, and are discharged through culverts G-306 A through J and into the discharge canal. This discharge is then conveyed to WCA-1 via this canal and via pump station G-310. Flows through treatment cells 1 through 4 are conveyed in a southerly direction through G-252 and G-253 (cells 1 and 3) and G-254, G-255, and G-256 (cells 2 and 4). Flows are discharged into WCA-1 via existing ENR Project collection canals, existing pump station G-251, and, under some conditions (when ENR Project outflows exceed the G-251 pump capacity of 450 cfs), through structures G-258, G-259, G-308, and G-309 into discharge canal and pump station G-310. Thus, there are two primary discharge locations for STA-1W into the L-7 canal located in the Refuge.

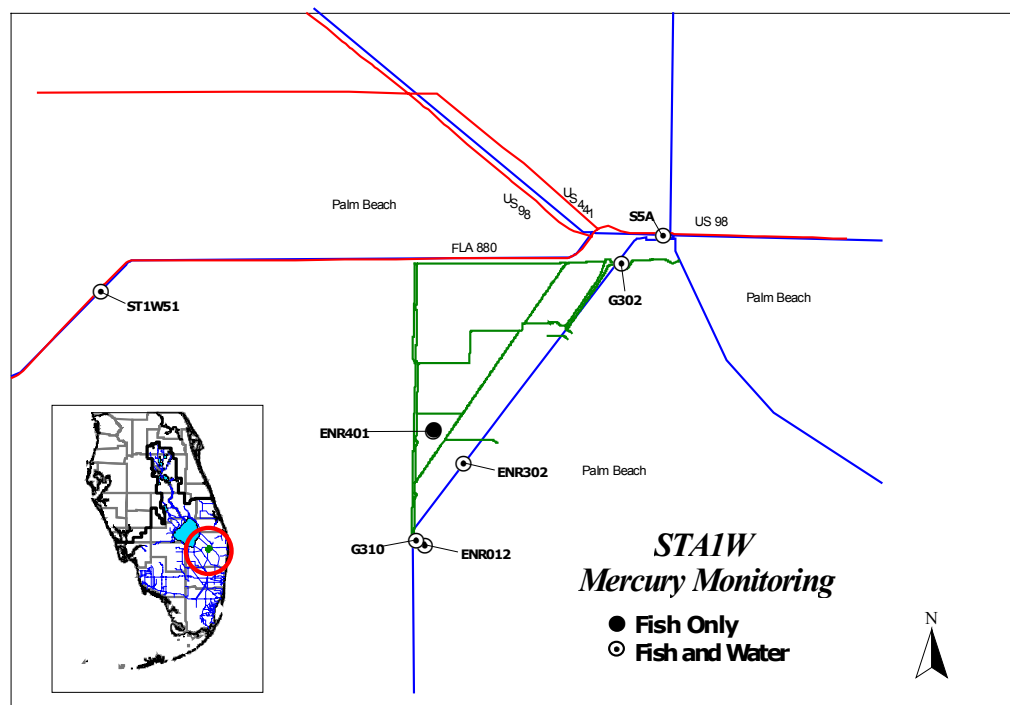


Figure 3. STA-1W monitoring sites

STA-2

STA-2 is located in western Palm Beach County near the Browns Farm Wildlife Management Area. STA-2 was developed to provide a total effective treatment area of 6,430 acres (cell 1 is 1,990 acres; cells 2 and 3 are 2,220 acres each; for additional details see SFWMD, 1999a). STA-2 is intended to treat discharges from the S-6/S-2 basin, the S-5A basin, the East Shore Water Control District, 715 farms, and Lake Okeechobee via pump stations S-6 and G-328. S-6 will serve as the primary supply canal pumping station, with G-328 serving as both an irrigation and “secondary” supply canal source from and to the STA supply canal (**Figure 4**). G-328 serves an approximated 9,980 acres of adjacent agricultural lands. Discharges from the supply canal are then conveyed southward to the Supply Canal, which extends across the northern perimeter. A series of supply canal culverts will then convey flows from the supply canal to the respective treatment cells (G-329 A through D into cell 1; G-331 A through G into cell 2; G-333 A through E into cell 3). Flows will travel southward through the treatment cells, eventually discharging to the discharge canal via culverts or gated spillways (culverts G-330 A through E from cell 1; gated spillway G-332 from cell 2; gated spillway G-334 from cell 3). Flows then travel eastward in the discharge canal to the STA-2 outflow pump station, G-335, which in turn conveys water to a short stub canal leading to the L-6 borrow canal. Water in the L-6 borrow canal will travel north, and then east into WCA-2A through six box culverts (each with a capacity of 300 cfs, invert at 12 ft) located east of G-339 about three miles south of S-6. The area to receive discharge was previously identified as a nutrient-impacted area. Under high-flow conditions, when stage in the L-6 canal exceeds 14.25 ft, water in the L-6 borrow canal will spill into five 72-inch cans and travel south toward S-7. Approximately 0.75 miles north of S-7, the berm has been degraded to an elevation of approximately 12 ft, allowing water to sheetflow into WCA-2A. Here again, the area to receive discharge was previously identified as a nutrient-impacted area.

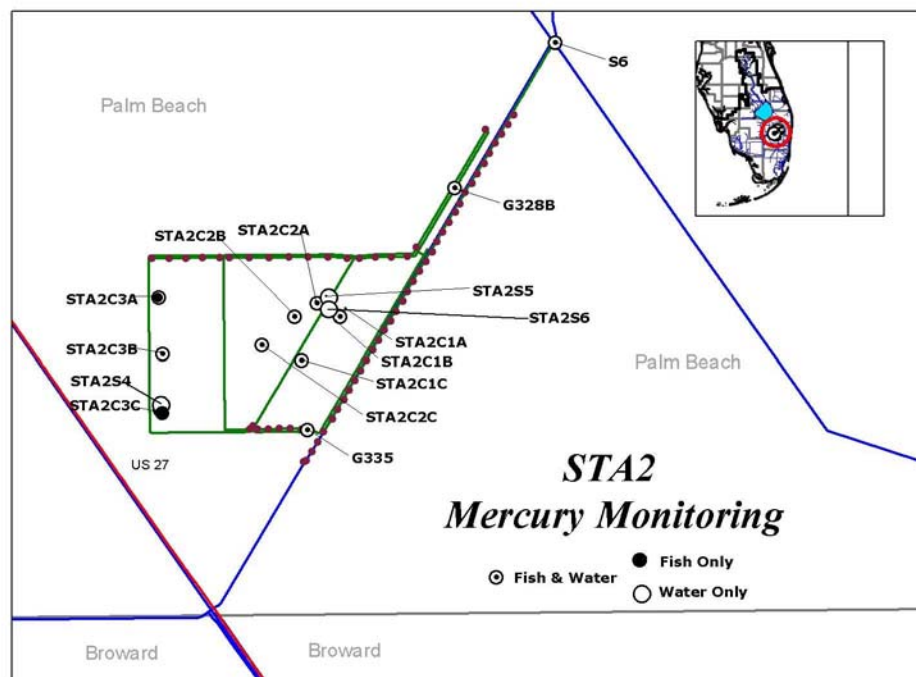


Figure 4. STA-2 monitoring sites

SUMMARY OF THE MERCURY MONITORING AND REPORTING PROGRAM

The monitoring and reporting program summarized below is described in detail in the “Mercury Monitoring and Reporting Plan for the Everglades Construction Project, the Central and Southern Florida Project, and the Everglades Protection Area”, which was submitted by the District to the Florida Department of Environmental Protection (FDEP), the U.S. Environmental Protection Agency (USEPA), and the U.S. Army Corps of Engineers (USACE) in compliance with the requirements of the aforementioned permits. The details of the procedures to be used in ensuring the quality of and accountability for the data generated in this monitoring program are set forth in the District’s Quality Assurance Project Plan (QAPP) for the Mercury Monitoring and Reporting Program, which was approved on issuance of the permit by the FDEP. QAPP revisions were approved by the FDEP on June 7, 1999.

EVERGLADES MERCURY BASELINE MONITORING AND REPORTING REQUIREMENTS

Levels of THg and MeHg in the pre-operational soils of each of the STAs and various compartments (media) of the downstream receiving waters define the baseline condition from which to evaluate mercury-related changes, if any, brought about by the operation of the STAs. The pre-ECP mercury baseline conditions are defined in the Everglades Mercury Background Report, which summarized all of the relevant mercury studies conducted in the Everglades through July 1997, during the construction, but prior to the operation of, the first STA. Originally prepared for submittal in February 1998, it was revised to include the most recent data released by the USEPA and the U.S. Geological Survey (USGS) and was submitted in February 1999 (FTN Associates, 1999).

PRE-OPERATIONAL MONITORING AND REPORTING REQUIREMENTS

Prior to completion of construction and flooding of the soils of each STA, the District is required to collect 10-cm core samples of soil at six representative interior sites and analyze them for THg and MeHg. Prior to initiation of discharge, the District is also required to collect biweekly samples of supply canal and interior water for analysis for THg and MeHg concentrations. When concentrations at the interior sites are found not to be significantly greater than that of the supply canal, this information is reported to the permit-issuing authority, and the biweekly sampling can be discontinued. Discharge begins after all the startup criteria are met.

This is followed by a stabilization period for both phosphorus and mercury. During this stabilization period, the release of stored phosphorus and mercury from flooded farm fields soils is anticipated, with concomitant instances of outflow or interior concentrations exceeding Supply Canal concentrations. As the bioavailable phosphorus and mercury are transported from the soil reservoir to the colonizing plants and accreting marsh soils, the magnitude, duration, and frequency of such phenomena will decrease until stabilization is achieved and the outflow and interior concentrations are routinely less than the supply canal on an annual basis. The stabilization period ends when the 12-month moving, flow-weighted average total phosphorous (TP) concentration in the outflow is less than 50 ppb. Most of the STAs complete this stabilization period within two years of initiation of flow-through operation.

OPERATIONAL MONITORING

Following approval for initiation of routine operation of an STA and thereafter, the permits require that the following samples be collected at the specified frequencies and analyzed for specified analytes:

Water: Quarterly, 500-ml unfiltered grab samples of water will be collected in pre-cleaned bottles using ultra-clean technique at the supply canals and outflows of each STA and will be analyzed for MeHg and THg (includes the sum of all mercury species in sample, e.g., Hg^0 , Hg^{I} , and Hg^{II} , as well as organic mercury). THg results will be compared with the Florida Class III Water Quality Standard of 12 ng/L to ensure compliance. Outflow concentrations of both THg and MeHg will be compared to concentrations at the supply canal.

Sediment: Triennially, six 10-cm sediment cores will be collected at representative interior sites and homogenized. The homogenate will be analyzed for THg and MeHg.

Prey fish: Semi-annually, a grab sample of between 100 and 250 mosquitofish (*Gambusia* sp.) will be collected using a dipnet at the supply canal sites, interior sites, and outflow sites of each STA and will be homogenized. The homogenate is to be subsampled in quintuplicate, and each subsample is to be analyzed for THg. On March 5, 2002 the FDEP approved a reduction in the number of replicate analyses of the homogenate from five to three (correspondence from F. Nearhoof, FDEP) based on a statistical analysis that demonstrated no significant difference that was appended to the District's petition letter (REF).

Top predator fish: Annually, 20 largemouth bass will be collected primarily via electroshocking methods at representative supply canal and discharge canal sites and representative interior sites in each STA. The fish muscle (fillet) will be analyzed for THg as an indicator of potential human exposure to mercury.

In 2000 the District began routine collection of sunfish at the same frequency, intensity (i.e., $n = 20$) and locations as largemouth bass. This permit revision fulfilled a USFWS recommendation (USFWS recommendation 9b in USACE Permit No. 199404532; for details, see correspondence to Bob Barron, USACE, dated July 13, 2000). Sunfish (analyzed as whole fish) also serve as a surrogate for attempts to monitor mercury in wading birds that do not nest in the STAs (for details on the monitoring program tracking mercury in wading birds in downstream areas, see **Appendix 2B-3** of the 2003 Everglades Consolidated Report). The addition of sunfish to the compliance monitoring program was approved by the FDEP on March 5, 2002 (correspondence from F. Nearhoof, FDEP).

It is important to note that virtually all (> 85 percent) of the mercury in fish tissues is in the methylated form (Grieb et al., 1990; Bloom, 1992; SFWMD, unpublished data). Therefore, the analysis of fish tissue for THg, which is a more straightforward and less-costly procedure than for MeHg, can be interpreted as being equivalent to the analysis of MeHg. Further details regarding rationales for sampling scheme, procedures, and data reporting requirements are set forth in the Everglades Mercury Monitoring Plan revised in March 1999 (Appendix 1 of QAPP, June 7, 1999).

QUALITY ASSURANCE MEASURES

For a quality assurance/quality control assessment of the District's Mercury Monitoring Program during the reporting year, see **Appendix 2B-3**.

STATISTICAL METHODS

As stated earlier, monitoring Hg concentrations in aquatic animals provides several advantages; however, interpretability of residue levels in animals can sometimes prove problematic due to the confounding influences of age or species of collected animals, or changes in range associated with changes in environmental conditions (e.g., marsh hydroperiod). For comparison, special procedures are used to normalize the data. Standardization is a common practice (Wren and MacCrimmon, 1986; Hakanson, 1980). To be consistent with the reporting protocol used by the FFWCC (Lange et al., 1998, 1999), mercury concentrations in largemouth bass were standardized to an expected mean concentration in three-year-old fish at a given site by regressing mercury against age (hereafter symbolized as EHg3; see Lange et al., 1999 and references therein). To adjust for the month of collection, otolith ages were first converted to decimal age using protocols developed by Lange et al., (1999). Sunfish were not aged. Consequently, age normalization was not available. Instead, arithmetic means were reported. However, efforts were made to estimate a least square mean (LSM) Hg concentration based on the weight of the fish. Additionally, the distribution of the different species of *Lepomis* (warmouth, *L. gulosus*; spotted sunfish, *L. punctatus*; bluegill, *L. macrochirus*; red ear sunfish, *L. microlophus*) collected during electroshocking was also considered as a potential confounding influence on Hg concentrations prior to each comparison.

Where appropriate, analysis of covariance (ANCOVA; SAS GLM procedure) was used to evaluate spatial and temporal differences in mercury concentrations, with age (largemouth bass) or weight (sunfish) as a covariate. However, use of ANCOVA is predicated on several critical assumptions (for review see ZAR, 1996), including:

1. That regressions are simple linear functions
2. That regressions are statistically significant (i.e., non-zero slopes)
3. That the covariate is a random, fixed variable
4. That both the dependent variable and residuals are independent and normally distributed
5. That slopes of regressions are homogeneous (parallel)

Regressions also require that collected samples exhibit a relatively wide range of covariate, that is, that fish from a given site are not all the same age or weight. Where these assumptions were not met, ANCOVA was inappropriate. Instead, standard ANOVAs or student's "t" tests (SigmaStat, Jandel Corporation, San Rafael, Calif.) were used. Possible covariates were considered separately and often qualitatively. The assumptions of normality and equal variance were tested by the Kolmogorov-Smirnov and Levene Median tests, respectively. Datasets that either lacked homogeneity of variance or departed from normal distribution were natural-log transformed and re-analyzed. If transformed data met the assumptions, they were used in ANOVA. If they did not meet the assumptions, then raw data sets were evaluated using non-parametric tests, such as the Kruskal-Wallis ANOVA on ranks or the Mann-Whitney Rank sum test. If the multigroup null hypothesis was rejected, groups were compared using either Tukey HSD or Dunn's method.

MONITORING RESULTS

PRE-OPERATIONAL MONITORING

STA-6, Section 1

As previously reported (SFWMD 1998c), STA-6, section 1 met startup criteria for mercury in November 1997 and began operation in December 1997.

STA-5

As reported in last year's Everglades Consolidated Report (Rumbold et al., 2001), STA-5 met startup criteria for mercury in September 1999.

STA-1W

As reported in last year's Everglades Consolidated Report (Rumbold et al., 2001), the permit for STA-1W was issued on May 11, 1999. STA-1W passed startup criteria during the week of January 17, 2000; flow-through operations began in early February 2000.

STA-2

STA-2 cells 2 and 3 met both mercury startup criteria on September 26, 2000 and November 9, 2000, respectively. Cell 1 still has not met the startup criteria as of this writing. See **Appendix 4B-2** for results of startup mercury monitoring of STA-2, including results from an expanded sampling program.

OPERATIONAL MONITORING

STA-6

Routine monitoring of mercury levels at STA-6 began in the first quarter of 1998. Results of monitoring prior to April 30, 2001 have been reported previously (SFWMD 1998c; 1999c; Rumbold and Rawlik, 2000; Rumbold et al., 2001a; Rumbold and Fink, 2002).

As is evident from data shown in **Tables 1** and **2**, which is graphically presented in **Figure 5**, concentrations of THg and MeHg spiked in STA-6 outflows during the second quarter of 2001. On June 20, 2001 the day of sample collection, the concentration of THg and MeHg reached 7.0 ng/L and 3.4 ng/L, respectively, at the outflow culvert of cell 3. As discussed in earlier reports (Rumbold et al., 2001a), proper interpretation of these data must consider hydrologic factors that can affect net MeHg production. From late May through early June 2001, STA-6 had experienced a drydown for at least 27 days in cell 3 and for at least 31 days in cell 5. The STA was then reflooded after receiving 5.3 inches of rain that fell in the area from May 31 to June 20.

STA-6 Surface Water

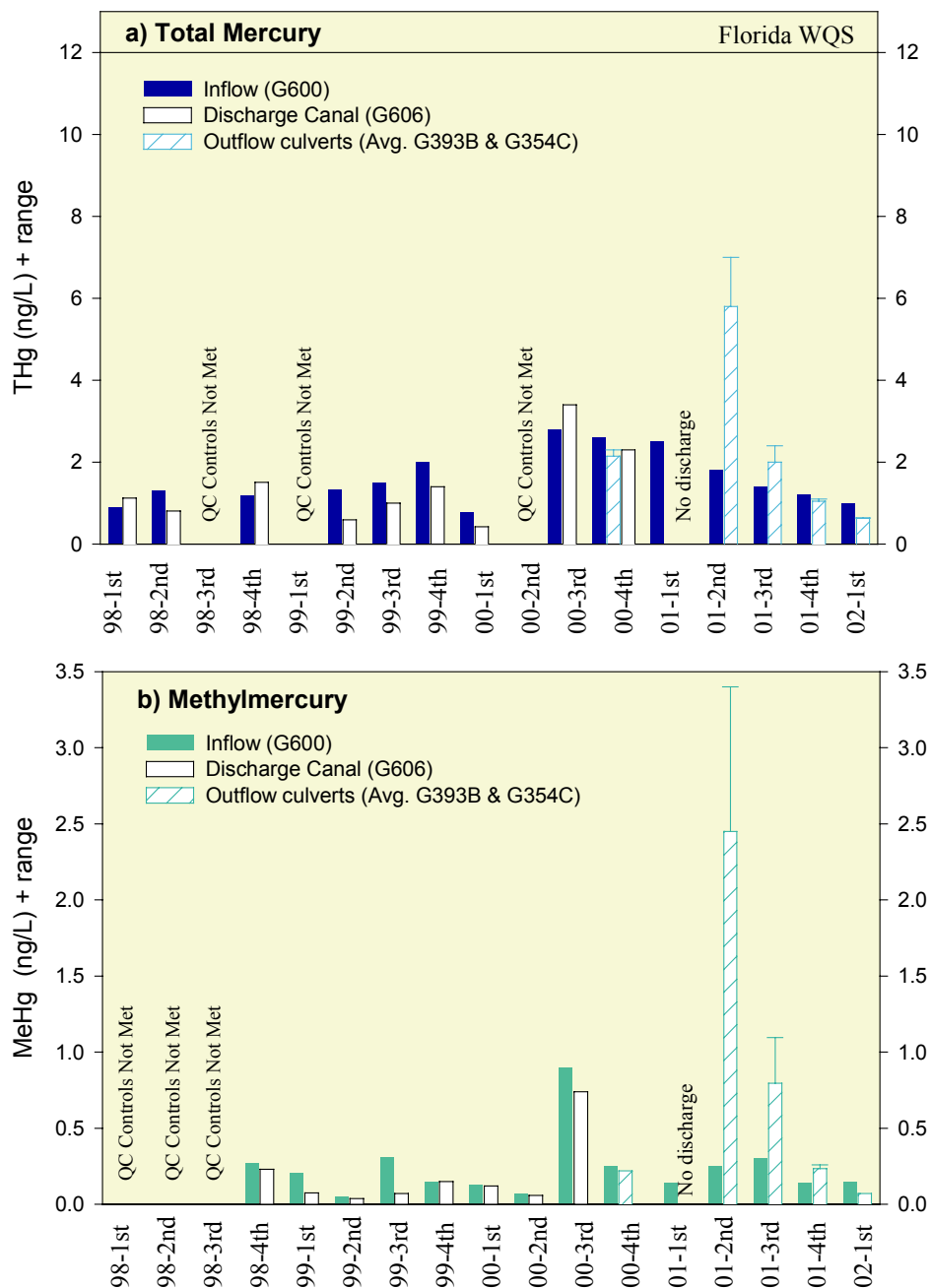


Figure 5. Concentration of (a) total mercury and (b) methylmercury in unfiltered surface water collected at STA-6

This sequence of events (drydown and reflooding with direct rainfall, which contains elevated levels of bioavailable inorganic mercury) likely contributed to the observed spike in both THg and MeHg (for details on the effect of drydown and oxidation on sediment mercury biogeochemistry and MeHg production (see Krabbenhoft and Fink, 2001). It is noteworthy that the concentration of THg declined to typical levels by the next quarter. MeHg also declined, albeit more slowly (**Figure 5**). By the first quarter of 2002, both THg and MeHg exhibited a negative percent change across the STA (**Table 1**). At no time during the reporting year did THg concentration exceed the Class III Water Quality Standard of 12 ng/L.

To conserve resources, the mercury monitoring plan for STA-6 was designed to provide information to assist in monitoring inflow versus outflow concentrations and bioaccumulation in fishes and to evaluate compliance with state water quality standards. It was not designed to provide the level of detail necessary to complete a mass balance. This type of analysis is very costly and requires measurements of all flows, fluxes, and storages, including local atmospheric deposition (wet and dry), evasion back to the atmosphere, groundwater flux, burial, storage in biomass, etc. Nevertheless, to bound the magnitude of the loads to and from the STA, a scoping-level assessment was carried out using the available data for the third and fourth quarters. (Because it would have required linear interpolation over a six-month period, loads were not calculated for the second quarter 2001; data were also not available for the second quarter of 2002 to allow for interpolation of surface water concentrations).

The results of this scoping-level assessment suggest that during the third quarter, inflow load of THg was 31 g, compared to an outflow load of 33 g (**Table 3**). When estimates of atmospheric loading of THg to the STA are considered (**Table 3**), it is easy to account for a gain and export of 2 g of THg from the STA (based on measurements at the Mercury Deposition Network station located at the ENR Project). During the fourth quarter, loading at the inflow pump of STA-6 was 28 g, whereas outflow load was only 19 g. Thus, even when ignoring the input of wet (Guentzel, 1997) and dry (USEPA, 1997) atmospheric deposition, the STA did not export, and likely stored, a significant quantity of inorganic mercury, though some of the apparent storage may have been lost to open-water or plant-mediated evasion of elemental mercury (Lindberg and Meyers, 1999). More importantly, the scoping-level assessment suggests that during the third quarter, which was bracketed by spikes in water column MeHg concentration (**Figure 5**), the inflow load of MeHg was 6 g, whereas the outflow load was 13 g. While atmospheric loading is considered the most significant source of inorganic mercury, it is generally thought to be minimal in terms of MeHg (**Table 3**, again based on MDN located at the ENR Project. T. Atkeson, personal communication). Therefore, it is difficult to account for the gain in MeHg unless there is substantial conversion of inorganic Hg to MeHg within the STA. While the outflow load of MeHg was much reduced during the fourth quarter, it was again greater than inflow load (**Table 3**). This is in sharp contrast to what was previously observed at the ENR Project, which was estimated to have a 68-percent removal efficiency for MeHg in the period 1995 through 1998 (Fink, 2000). To reduce uncertainties and improve load estimates, expanded mercury monitoring, including biweekly sample collection, has been proposed for STA-6. This will reduce the period over which concentrations must be interpolated and will also reduce load error associated with concentration error.

Table 1. Concentrations of total mercury (THg) and methylmercury (MeHg) in surface waters collected quarterly from the STAs (units ng/L)

STA	THg (ng/L)						MeHg (ng/L)				%MeHg	
	Quart	Inflow	Remark*	Outflow	remark	THg WQS ¹	Inflow	remark	Outflow	remark	Inflow	Outflow
A 6**	01-2	1.80		5.80		<WQS	0.25		2.45		14%	41%
	01-3	1.40		2.00		<WQS	0.30		0.80		21%	38%
	01-4	1.20		1.05		<WQS	0.14		0.24		12%	22%
	02-1	1.0		0.63		<WQS	0.15		0.07		15%	12%
A 52	01-2	2.50		2.10		<WQS	0.74		0.49		31%	22%
	01-3	2.93		1.52		<WQS	0.52		0.20		18%	11%
	01-4	1.09		0.95		<WQS	0.17		0.23		16%	24%
	02-1	1.09		0.48		<WQS	0.16		0.09		14%	21%
A1W [§]	01-2	2.6	J5	1.3	J5	<WQS	0.10		0.06		NC	NC
	01-3	3.50		1.17		<WQS	0.46		0.18		13%	16%
	01-4	1.20		0.86		<WQS	0.25		0.12		21%	14%
	02-1	1.40		1.08		<WQS	0.21		0.10		15%	10%

* For qualifier definitions, see FDEP rule 62-160: "A" - averaged value; "U" - undetected, value is the MDL; "I" - below PQL; "J" - estimated value, the reported value failed to meet established QC criteria; "J3" - estimated value, poor precision, "V" - analyte detected in both the sample and the associated method blank.

¹ Class III Water Quality Standard of 12 ng THg / L.

** Outflow sampling site for STA 6 was moved from G606 to G354C and G393B culverts and, thus, reported values represent mean.

[†] "NC" – not calculated; "NO" – no outflow at the time of sampling.

² STA 5 has multiple inflows and outflows and reported value represents mean of valid data (unqualified).

[§] STA 1W has a single inflow and two outflows; the reported value for the latter represents mean of valid data (unqualified).

Table 2. Percent change in concentration of THg and MeHg in surface water across STAs (i.e., outflow-inflow/inflow)

STA	Quarter	THg	MeHg
STA 6	01-2	222%	880%
	01-3	43%	167%
	01-4	-13%	71%
	02-1	-37%	-53%
Annual average		54%	266%
Cumulative average		6%	64%
STA 5	01-2	-16%	-34%
	01-3	-48%	-62%
	01-4	-13%	35%
	02-1	-56%	-44%
Annual average		-33%	-26%
Cumulative average		4%	13%
STAIW	01-2	NC	-40%
	01-3	-67%	-61%
	01-4	-28%	-52%
	02-1	-23%	-52%
Annual average		-39%	-51%
Cumulative average		-34%	-7%

** Only valid (unqualified) data used in calculations; see Table A4-1.2 for raw data and qualifiers.

Table 3. Scoping-level assessment of THg and MeHg loads at STA-6

Constituent	Quart	Inflow load (g)	Flow-wt Inflow Conc. (ng/L)	Rainfall deposition (g)	Outflow load (g)			Flow-wt Outflow Conc.(ng/L)
					Cell 5	Cell 3	Total	
THg	3 rd	31	1.48	23.0	16	17	33	2.62
	4 th	28	1.27	7.7	11	8	19	1.46
MeHg	3 rd	6	0.28	0.87	5	8	13	1.02
	4 th	4	0.20	0.13	3	3	6	0.47

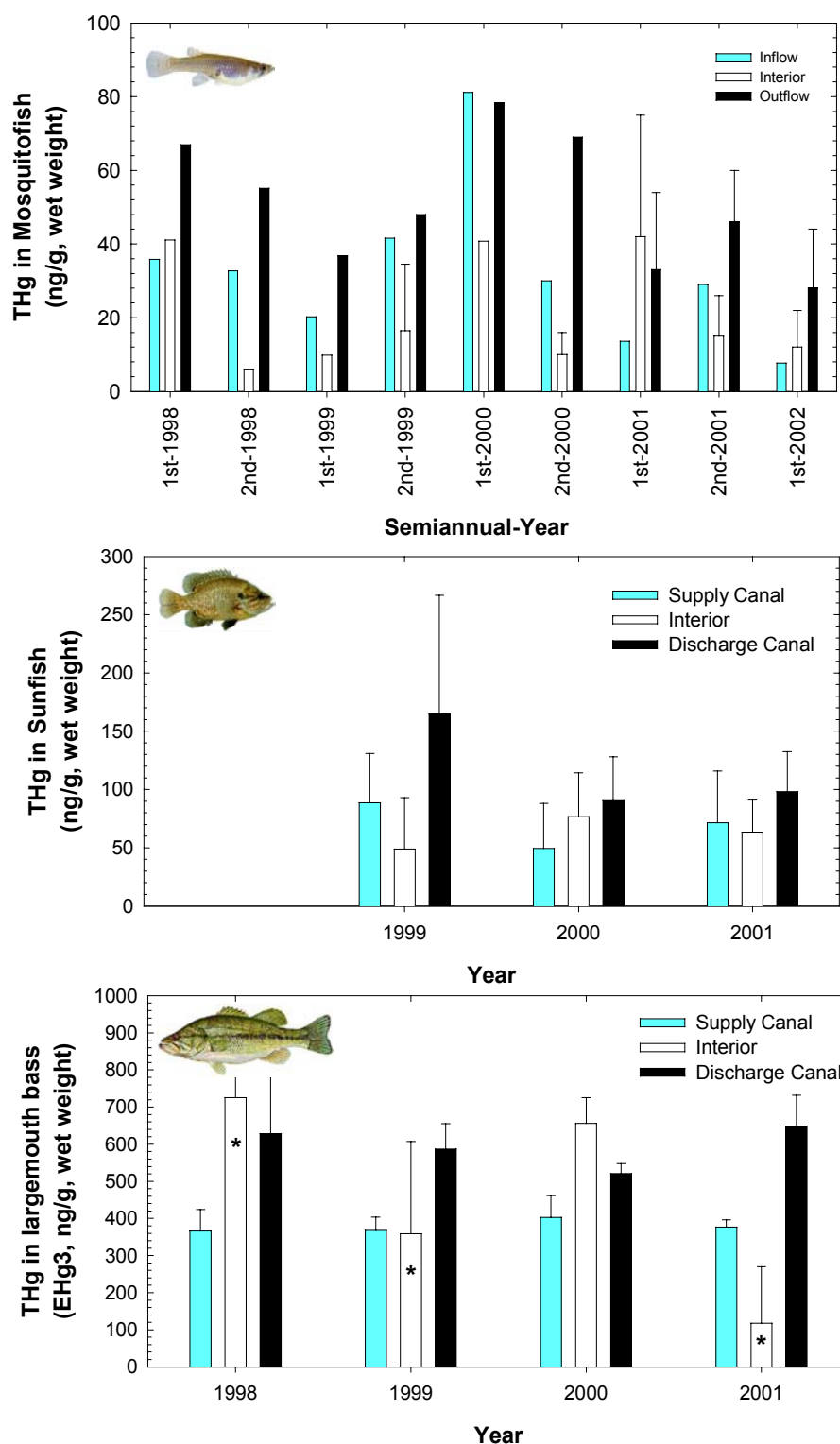


Figure 6. Mercury concentrations in (a) mosquitofish composites; (b) whole sunfish; and (c) fillets of largemouth bass collected at STA-6. Note: The latter are reported as the expected concentration in a three-year-old fish, EHg3, unless this could not be calculated (*, for details, see Table 5), in which case, the arithmetic mean is reported

Levels of mercury in mosquitofish have continued to decline from a peak concentration that occurred in fish collected during the first semiannual event in 2000 (**Figure 6**). This is particularly noteworthy given the spike in MeHg that occurred in surface water during the second quarter of 2001. As is evident from **Figure 6**, there was no evidence that the spike in water column MeHg was followed by significant increases in mercury bioaccumulation at any trophic level.

As was discussed in the *2002 Everglades Consolidated Report*, the outflow collection site was moved in early 2001 from G-606 to G-393B and G-354C. As is evident from the range bars shown in **Figure 6**, mosquitofish from the two outflow culverts differed substantially in THg concentrations. Mosquitofish collected at the outflow of cell 5 (G-345C) continued to have lower concentrations of THg compared to fish from the outflow of cell 3 (G-393B). This difference was consistent with that observed in mosquitofish collected from the interior of each cell, that is, levels were lower in fish from the interior of cell 5. (For a review of between-cell differences in STA-6, see Rumbold et al., 2001b). Based largely on levels in fish from the cell 3 outflow culvert, mosquitofish continued to exhibit a positive percent change in THg across the STA (**Table 4**).

Similar to mosquitofish, visual inspection of the data presented in **Figure 6** suggests that sunfish from the STA-6 discharge canal consistently contained greater concentrations of Hg than fish from the supply canal. In 2001 this difference was statistically significant ($H = 18.1$, $df = 3$, $p < 0.001$; Dunn's post-hoc test $p < 0.05$). Sunfish, therefore, exhibited a positive percent change in Hg across the STA (**Table 5**). Sunfish from the discharge canal also contained greater Hg levels than fish from cell 5 (Dunn's post-hoc test, $p < 0.05$), but did not differ from fish from cell 3 ($p > 0.05$). It is important to note that neither location-related differences in total length, which were not significant (ANOVA; $df = 3, 62$; $F = 2.3$; $p = 0.08$), nor species composition of sampled fish appeared to be sufficient to account for spatial patterns in Hg burdens. Visual inspection of the data presented in **Figure 6** also suggests that Hg in sunfish from the STA-6 discharge canal has declined since 1999. However, the size of these fish has also declined from 1999, and this may account for the apparent declines in Hg burdens.

Results from operational monitoring of mercury concentrations in largemouth bass from STA-6 are summarized in **Table 6** and are graphically displayed in **Figure 6** (values for individual fish are provided in **Table 1** at the end of this appendix, to be added later). Similar to mosquitofish and sunfish, largemouth bass collected during the last four years at STA-6 showed higher tissue mercury concentrations from the discharge canal compared to the supply canal (i.e., positive percent change; **Table 6** and **Figure 6**). Previously, this difference in Hg concentration between fish caught in the supply canal and the discharge canal has been shown to be significant by ANCOVA, which can partition the effects of differences in age. In 2001, Hg concentrations in fish collected from the supply canal and the discharge canal again differed significantly (ANCOVA; $df = 1, 37$; $F = 28.31$; $p < 0.001$). Because of an interaction between the effects of fish age and location on mercury concentration, ANCOVA could not be used to assess spatial patterns in Hg levels in bass collected in the interior versus the supply canal or discharge canal.

In terms of temporal trends, as reported last year (Rumbold and Fink, 2002) Hg in bass collected from the discharge canal had declined since 1998 (ANCOVA, $df = 1, 37$; $F = 8.8$; $p = 0.005$). In 2001, Hg in bass from the discharge canal increased and were no longer significantly different from values observed in 1998 ($df = 1, 37$; $F = 0.03$; $p = 0.86$) and thus the trend of decreasing Hg was reversed.

Table 4. Concentration of total mercury (THg) in mosquitofish composites collected semi-annually from STAs (units ng/g wet weight)

STA	Half-year	Inflow fish	Interior fish	Outflow fish	Percent change
STA 6	2001-2	29	15 ±11	46 ±14	59%
	2002-1	8	12 ±10	28 ±16	250%
	Annual mean	18	14	37	106%
	Cumulative mean	32 ±21	21 ±15	51 ±17	59%
STA 5	2001-2	40 ±3	15 ±2	49 ±28	23%
	2002-1	36 ±5	16 ±10	32 ±14	-11%
	Annual mean	38	16	41	8%
	Cumulative mean	39 ±4	38 ±32	38 ±16	-3%
STA 1W	2001-2	23	14 ±18	11 ±5	-52%
	2002-1	10	7 ±7	5 ±0.1	-50%
	Annual mean	16	10	8	-50%
	Cumulative mean	21 ±8	16 ±6	16 ±12	-24%

* Mosquitofish are collected semi-annually at inflow, interior and outflow sites.

1 - Standard deviation is reported where multiple composites are collected from location (e.g., multiple inflows or outflows, multiple cells); range is reported where two sites are sampled; other values represent mean of five analyses of a single composite sample.

Note: per FDEP approval (March 5, 2002), the number of aliquots was reduced from 5 to 3.

Note: per FDEP approval (March 5, 2002), collection locations were reduced from 4 to 2 for both the inflow and outflow of STA 5.

2 - Percent change = outflow-inflow / inflow

Table 5. Concentration of total mercury (THg, ng/g wet weight) in sunfish (*Lepomis* spp.) collected from STAs in 2001 (sample size in parentheses)

STA	Inflow fish	Interior fish	Outflow fish	Percent change
STA 6	72 ±44 (20)	63 ±27.5(261)	98 ±34(20)	36%
Cumulative mean*	70 ±44(59)	66 ±38(88)	118 ±73(60)	69%
STA 5	63 ±22(20)	150 ±66(391)	116 ±44(20)	84%
Cumulative mean*	82 ±46 (61)	113 ±107 (120)	104 ±67(53)	27%
STA 1W	31 ±17 (20)	16 ±17 (461)	39 ±26 (391)	26%
Cumulative mean*	42 ±22 (58)	25 ±29 (155)	30 ±21 (99)	-29%

* Sunfish collected in 1999, prior to permit revision or STA operation (in the case of STAs 5 and 1W) were included in the cumulative average.

1 - Where n > 20; multiple sites were sampled and pooled, i.e., multiple interior or outflows

2 - Percent change = outflow-inflow / inflow

Table 6. Standardized, EHg3 \pm 95%, and arithmetic mean concentration (mean \pm 1SD, n; in parentheses) of total mercury (ng/g, wet weight) in fillets from largemouth bass collected at STAs in 2001

STA	Inflow fish	Interior fish	Outflow fish	Percent change ²	Consumption advisory exceeded
STA-6	377 \pm 19 (253 \pm 91, 20)	NC (2) (118 \pm 152, 9)	649 \pm 83 (585 \pm 247, 20)	72%	Yes
Cumulative mean	378(a)	516(b)	596(a)	58%	
STA-5	NC (2) (290 \pm 130, 20)	801 \pm 147 (489 \pm 197, 401)	NC (1) (475 \pm 133, 20)	64%	Yes
Cumulative mean*	294(b)	403(b)	440(b)	50%	
STA-1W	NC (1) (371 \pm 156, 20)	77 \pm 24 (61 \pm 51, 201)	NC (1) (118 \pm 73, 261)	-68%	No
Cumulative mean*	279(b)	79(b)	91(b)	-67%	

* Bass collected in 1999 prior to operation of STAs 5 and 1W were included in the cumulative average (a) based on EHg3, or (b) based on arithmetic mean.

1 - Where n > 20; multiple sites were sampled and pooled, i.e., multiple interior or outflows.

2 - Percent change = outflow-inflow / inflow.

¶ Florida limited consumption advisory threshold is 500 ng/g in three-year-old bass.

NC = not calculated, where: (1) regression slope was not significantly different from 0, or (2) poor age distribution of collected fish.

While **Figure 6** shows substantial variability in Hg levels in interior fish, this was a function of sampling location. In 2001, bass were collected only from cell 5 and, because of known between-cell differences, must be compared only to the three bass collected from cell 5 in 1999. In 1999, the bass had an average age of 2.8 years, whereas in 2001 bass were just 1.1 years old, indicating that the observed decrease in concentrations likely was age-related. More importantly, the apparent decline from 2000 to 2001 in Hg concentration in interior fish was likely a between-cell difference.

Levels of mercury in fish tissues can also be put into perspective and evaluated with regard to a mercury risk to wildlife. The U.S. Fish and Wildlife Service (USFWS) has proposed a predator protection criterion of 100 ng/g THg in prey species (Eisler, 1987). More recently, in its "Mercury Study Report to Congress," the USEPA proposed 77 ng/g and 346 ng/g for trophic level (TL) 3 and 4 fish, respectively, for the protection of piscivorous avian and mammalian wildlife (USEPA, 1997). STA-6 mosquitofish collected during the reporting year, which are considered to be at TL 2 to 3, depending on age (Loftus et al., 1998), contained Hg at concentrations less than the USFWS and USEPA criteria. Sunfish from STA-6, which are at TL 3 (*L. gulosus* at TL 4; Loftus et al., 1998), contained levels of Hg that approached or exceeded the EPA criteria but, on average, were less than the USFWS criteria. Similarly, after adjusting arithmetic mean Hg concentrations in largemouth bass fillets to whole-body concentrations (whole-body THg concentration = 0.69 x fillet THg; Lange et al., 1998), bass in the discharge canal of STA-6 exceeded the USEPA's guidance value for TL 4 fish. Alternatively, bass inhabiting the marsh of Cell 5 did not exceed the guidance value. Based on these criteria, there is some risk of adverse chronic effects from mercury exposure to fish-eating wildlife if feeding preferentially at STA-6.

Hg concentrations in fish collected from STA-6 were substantially greater (up to five times greater) than levels observed at STA-1W, which subsumed the prototype STA (the ENR Project) (**Table 6**). However, concentrations of Hg in STA-6 fishes were comparable to levels observed in other areas of the Everglades (**Appendix 4B-3**), and thus may reflect the overall mercury conditions in South Florida rather than being a consequence of STA operation.

STA-5

As stated above, STA-5 met startup criteria for mercury in September 1999; routine monitoring began during the first quarter of 2000. However, because of drought conditions and the detection of high phosphorus concentrations at the outflows, STA-5 did not begin flow-through operation until July 7, 2000. Results of monitoring prior to April 30, 2001 have been reported previously (Rumbold and Rawlik 2000; Rumbold et al. 2001a; Rumbold and Fink, 2002).

Soil cores were first collected from STA-5 in November 1998 prior to the flooding of the STA (Rumbold and Rawlik, 2000). Cores were collected again at the STA in November 2001 (**Table 7**). It is important to note that locations were changed in 2001 to more equally distribute sampling sites throughout the STA. Average concentration of THg in STA-5 sediments collected in 2001 did not differ from levels observed in 1998 (mean THg concentration in 1998 cores was 89.4 ± 23 ; t-test, $df = 10$; $t = 0.73$; $p = 0.48$) and continued to be within the expected range for Everglades soils (Delfino et al., 1993; Gilmour et al., 1998; Rumbold et al., 2001a). More importantly, the percentage of THg that was MeHg (**Table 7**), which is considered an index of *in situ* methylation, was within the expected range for Everglades sediments (Gilmour et al., 1998; C. Gilmour, personal communication).

Table 7. Total mercury (THg) and methylmercury (MeHg) concentration in STA soils (i.e., 10-cm depth composited; unit ng/g dry weight)

STA	Year	Station	THg	remark*	MeHg	remark	%MeHg
STA5	2001	Cell1A	15.8		0.288		1.8%
	2001	Cell2A	44.1		0.478		1.1%
	2001	Cell2B	80.7		0.378		0.5%
	2001	Cell2B	97.1		0.609		0.6%
	2001	Cell1B	105		2.12		2.0%
	2001	Cell1B	113		0.372		0.3%
	Mean		75.9	±38	0.71	±0.7	1.1%
STA1W	2002	ENR302	73.8		0.048	I	0.1%
	2002	ENR102	50.6		0.046	I	0.1%
	2002	ENR303	59.6		-0.038	U	NC
	2002	ENR401	61		-0.027	U	NC
	2002	ENR203	88.7		0.08	I	0.1%
	2002	ST1W51	80.3		0.222		0.3%
	Mean		69	±14	0.08	±0.07	1.1%

For qualifier definitions see FDEP Rule 62-160. Qualifiers: "A" - Averaged value; "U" - Undetected, value is the MDL; "I" - Below PQL; "J" - Estimated value, the reported value failed to meet established QC criteria; "J3" - Estimated value, poor precision; "V" - Analyte detected in both the sample and the associated method blank

Further, concentrations of MeHg in STA-5 sediments also did not differ between years (mean concentration \pm 1SD was 0.53 ± 0.22 ng/g in 1998; $df = 10$, $t = -0.58$, $p = 0.57$). However, because sampling locations were not identical in 1998 and 2001, comparisons between years must be interpreted with some caution.

As shown in **Table 1** and **Figure 7**, THg and MeHg in the water column were at a lower concentration in inflows and outflows during the second half of the reporting year. More importantly, MeHg in surface water has declined and has remained at low concentrations relative to the spike that occurred in the fourth quarter of 2000. Further, in all but one instance THg and MeHg exhibited a negative percent change across the STA (i.e., they were at a lower concentration at the outflow compared to the inflow; calculated using mean concentrations, not flow-weight averages; **Table 1**). The one instance where outflow exceeded inflow concentration occurred during the fourth quarter of 2001, when average MeHg concentration was 0.23 ng/L at the outflows and 0.17 ng/L at the inflows. Annual average percent change across the STA was -33 percent and -26 percent for THg and MeHg, respectively, which were improvements over the previous year. Thus, on average STA-5 was a sink for both constituents in its second full year of operation. At no time during the reporting year did THg concentration exceed the Class III Water Quality Standard of 12 ng/L.

Results from operational monitoring of mercury concentrations in STA-5 mosquitofish are summarized in **Table 4** and **Figure 8**. During the current reporting year, STA-5 mosquitofish from the interior marshes contained about 50 percent less Hg than fish from either the inflows or outflows. This is a decline from peak levels observed in interior mosquitofish during the second semi-annual event in 2000, which roughly coincided with the spike in MeHg in the water column (**Figure 8**). Similar to what was observed last year, mosquitofish from cell 1B (i.e., marsh and at outflow culverts) contained greater Hg burdens than fish from cell 2B. By comparison, Hg levels in mosquitofish at the outflows were similar to fish at the inflows, with the cumulative means suggesting a small percent change across the STA – positive during the first half and negative during the second half of the year. Hg concentrations in STA-5 mosquitofish were low relative to other Everglades areas.

Similar to sunfish caught in 2000, sunfish collected in 2001 from STA-5 also showed significant spatial variability in Hg levels (**Figure 8**, Kruskal-Wallis ANOVA on ranks; $df = 3$, $H = 34.6$, $p < 0.001$). Unlike mosquitofish, median Hg concentration in sunfish collected from the supply canal (58 ng/g) differed from that of fish caught in the discharge canal (115 ng/g) and from the interior (median was 110 ng/g in cell 1B, and 160 ng/g in cell 2B) (Dunn's post-hoc test); other pairwise comparisons were not significant (i.e., discharge canal versus interior, or cell 1B versus cell 2B fish). Consequently, sunfish exhibited a positive percent change in Hg concentrations across the STA (**Table 5**). It should be noted that the slightly higher Hg levels in fish collected from cell 2B relative to fish from cell 1B, observed in both 2000 and 2001, which is inconsistent with observed spatial patterns in water or mosquitofish (i.e., cell 1B typically higher than cell 2B) may have again been attributable to differences in fish weight that is used as an age surrogate. Fish from cell 2B were again significantly larger than fish from other sites (Tukey test, $p < 0.05$).

Interannual differences in Hg levels were found when results of sunfish caught from the interior and discharge canal were pooled ($H = 64.98$, $df = 2$, $p < 0.001$), with higher levels in 2000 and 2001 compared to 1999; fish collected in 2001 did not differ from 2000 fish (Dunn's method, $p < 0.05$).

STA -5 Surface Water

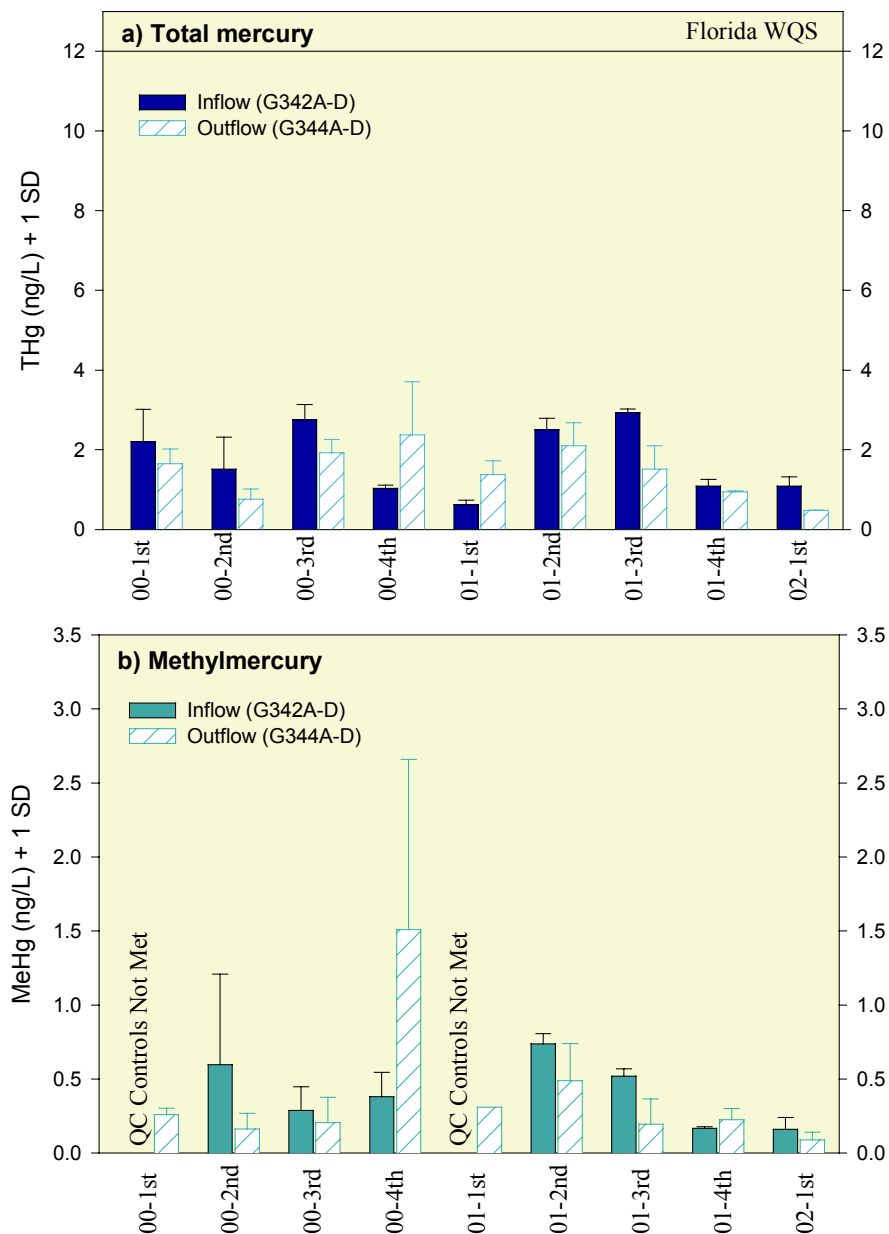


Figure 7. Concentration of (a) total mercury and (b) methylmercury in unfiltered surface water collected at STA-5

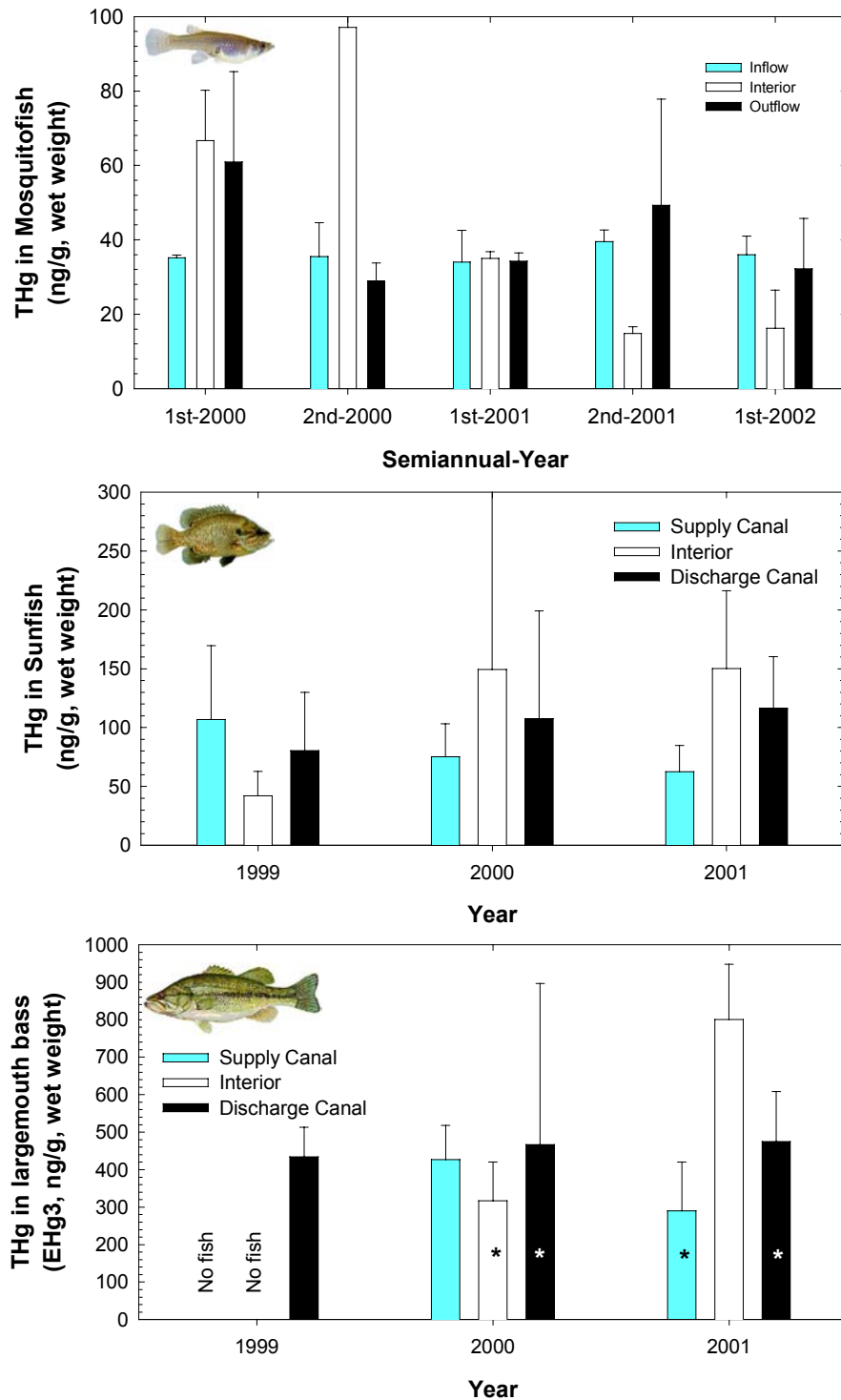


Figure 8. Mercury concentrations in (a) mosquitofish composites, (b) whole sunfish, and (c) fillets of largemouth bass collected at STA-5. Note: The latter are reported as the expected concentration in a three-year-old fish, EHg3, unless this could not be calculated (*for details see **Table 5**), in which case the arithmetic mean is reported

It should be noted that fish from the interior and the discharge canal increased in size in 2000, which may account for increased THg concentration; however, fish from the discharge canal decreased in size in 2001 (compared to 2000 and 1999), but exhibited no marked decline in Hg levels. It is possible, however, that the decrease in average body burden that would have been expected with a decrease in fish size may have been offset by a change in species composition and an increase in proportion of warmouth caught from the discharge canal.

By comparison, sunfish sampled from the supply canal, the population of which remained about the same size (Student-Newman-Keuls Method, $p < 0.05$) and species composition throughout the monitoring period, showed a general monotonic decrease in Hg from 1999 through 2001, with levels significantly different in 1999 and 2001 ($H = 9.3$, $df = 2$, $p = 0.01$; Dunn's method, $p < 0.05$); however, 2001 did not differ significantly from 2000 ($p > 0.05$).

The confounding influence that age has on tissue-Hg interpretation was also evident in largemouth bass collected at STA-5 in 2001 (**Table 6** and **Figure 8**). Spatial patterns are clearly present in arithmetic mean Hg concentrations (i.e., not normalized to age) shown in **Table 6**, with THg levels in supply canal bass less than interior bass that were greater than discharge canal bass. However, the average age of fishes was 1.8 years in the supply canal, 1.9 years in the interior, and 2.4 years in the discharge canal. If exposure was similar at all sites, one would expect that the older population in the discharge canal would have greater body burdens. However, this was not the case. Moreover, when tissue concentrations of interior fish were standardized to a three-year-old fish (i.e., EHg3), levels were much higher in interior fish compared to the arithmetic mean for fish from either the supply or discharge canals; EHg3 could not be estimated for discharge canal fish due to non-significant regression, nor could it be estimated for supply canal fish due to poor age distribution of the collected fish (almost all were age-class two years). It should be noted from **Figure 8** that sunfish from the interior marsh also contained elevated Hg levels relative to fish in the supply and discharge canals (refer to the above discussion regarding the size of sunfish from cell 2B). Similar to last year, the small range in the age of fishes collected from the interior of STA-5 allowed for the use of a simple rank sum test to examine between-cell differences in tissue Hg. Unlike last year, where between-cell differences were significant (with Hg in bass from cell 1 > cell 2), bass collected in 2001 from the two cells did not differ significantly in Hg concentrations (Mann-Whitney Rank sum test, $n = 20$, $T = 418$, $p = 0.83$).

Visual inspection of the data presented in **Figure 8** suggests that levels of Hg may have increased in interior bass. However, this graph may be somewhat misleading. The data presented for 2000 interior bass was an arithmetic average for first-year fish (EHg3 could not be estimated), whereas data for 2001 fish is reported as EHg3. Note that the *2002 Everglades Consolidated Report* raised the concern that, given the elevated arithmetic mean concentration in first-year fish, it was possible that older bass, if present in the interior marsh, would contain greater concentrations of Hg. This concern appears to have been confirmed by the data reported herein.

Data presented in **Figure 8** also suggest that levels of Hg have remained unchanged in fish in the discharge canal; however, this may also be somewhat misleading. The arithmetic mean concentration (475 ± 133 ng/g) was slightly higher in bass collected in 2001 that were, on average, 2.45 years old compared to the arithmetic mean concentration observed in the 2.75-year-old bass collected in 2000 (467 ± 430 ng/g) and the EHg3 of 1999 bass (434 ± 79 ng/g). Given the respective ages of the sampled populations, there appears to be some evidence of slightly increasing Hg concentrations in fish from the STA-5 discharge canal over the last three years. As reported above, this conclusion would be consistent with what has been observed in the sunfish at STA-5. However, unlike STA-6, STA-5 is still in its stabilization period, and such phenomena are expected and are not, as yet, a cause for undue concern.

In terms of a risk to fish-eating wildlife, levels of tissue Hg in mosquitofish collected during the reporting year were generally below the USEPA or USFWS guidance level. Likewise, after adjusting arithmetic mean Hg concentrations in largemouth bass fillets to whole-body concentrations (whole-body THg concentration = $0.69 \times$ fillet THg; Lange et al., 1998), STA-5 bass also did not exceed the EPA's guidance value for TL 4 fish (346 ng/g). Alternatively, Hg levels in sunfish, which are considered the best indicator of mercury exposure to fish-eating wildlife, slightly exceeded the USEPA and USFWS criteria. Thus, as with STA-6 there is some elevated risk to fish-eating wildlife feeding at STA-5.

As with fish at STA-6, fish collected from STA-5 generally contained greater Hg concentrations than did fish at STA-1W, which subsumed the prototype STA (the ENR Project). (**Table 6**). However, concentrations of Hg in fish from STA-5 were also comparable to levels observed in other Everglades areas (**Appendix 4B-3**), and thus may reflect overall mercury conditions in South Florida rather than a result of any changes brought on by operation of the STA.

STA-1W

Routine monitoring of mercury levels in surface waters of STA-1W began on February 16, 2000. Results of STA-1W monitoring prior to April 30, 2001 have been reported previously (Rumbold and Rawlik, 2000; Rumbold et al., 2001a; Rumbold and Fink, 2002).

Soil cores were first collected from STA-1W in January 1999, when STA-1W subsumed the ENR Project (Rumbold and Rawlik, 2000). Cores were collected at the same locations within STA-1W in January 2002 (**Table 7**). A paired t-test revealed no significant change in THg concentration from 1999 and 2002 ($df = 5$; $t = 2.345$; $p = 0.7$), with levels of THg in STA-1W sediments continuing to be within the expected range for Everglades soils (Delfino et al., 1993; Gilmour et al., 1998; Rumbold et al., 2001a). Alternatively, concentrations of MeHg in STA-1W sediment were relatively low compared to other Everglades areas. The relative low concentrations of MeHg were best illustrated by the percentage of THg that was MeHg (**Table 7**). This suggests little *in situ* production, i.e., conversion of inorganic mercury to MeHg. While MeHg concentrations could not be assessed statistically because of the number of "non-detects" (it should be noted that different laboratories analyzed the two sets of cores), visual inspection of the data does not reveal any marked temporal trends in levels. It is interesting to note that similar to what was observed in 1999, the core from STA-1W cell 5, i.e., the cell that was most recently constructed and operated, contained the highest concentration of MeHg.

As shown in **Table 1** and **Figure 9**, concentrations of both THg and MeHg in surface water at the outflows of STA-1W were consistently less than concentration of the corresponding constituent at the inflow. This spatial pattern is further illustrated by a persistent negative percent change across the STA (**Table 1**). This is consistent with the removal efficiency that was routinely observed for the ENR Project, which was subsumed by STA-1W (SFWMD 1999b).

Concentrations of THg in mosquitofish are summarized in **Table 4** and are graphically presented in **Figure 10**. Levels of mercury in mosquitofish from STA-1W were similar to, or have declined slightly, when compared to concentrations observed in fish collected previously from this area, when it was operated as the ENR Project (SFWMD, 1999b). Further, mercury levels in fish from STA-1W continue to be relatively low compared to other STAs (see discussions above) and the remainder of the Everglades (**Appendix 4B-3**).

STA 1W Surface Water

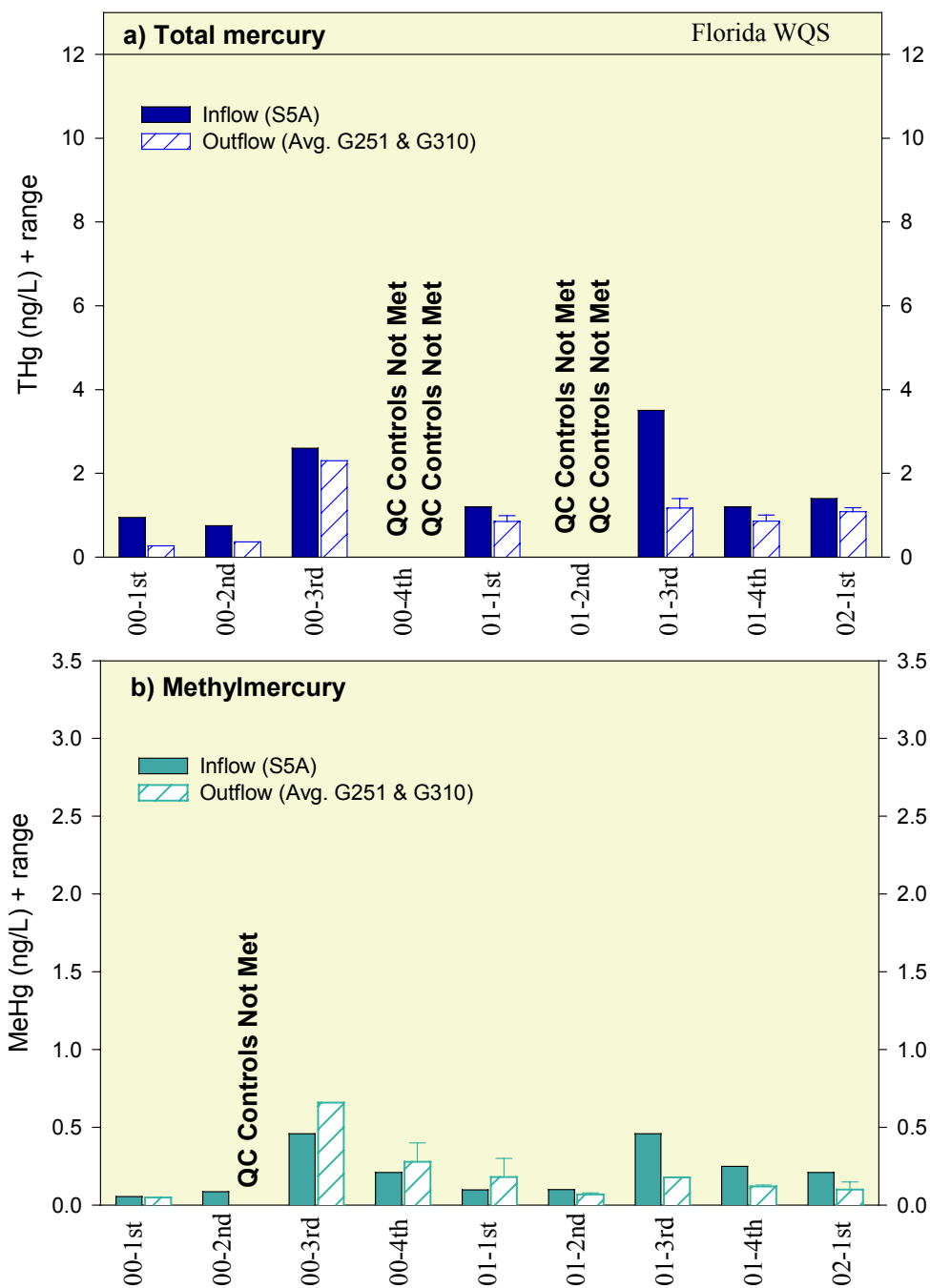


Figure 9. Concentration of (a) total mercury and (b) methylmercury in unfiltered surface water collected at STA-1W

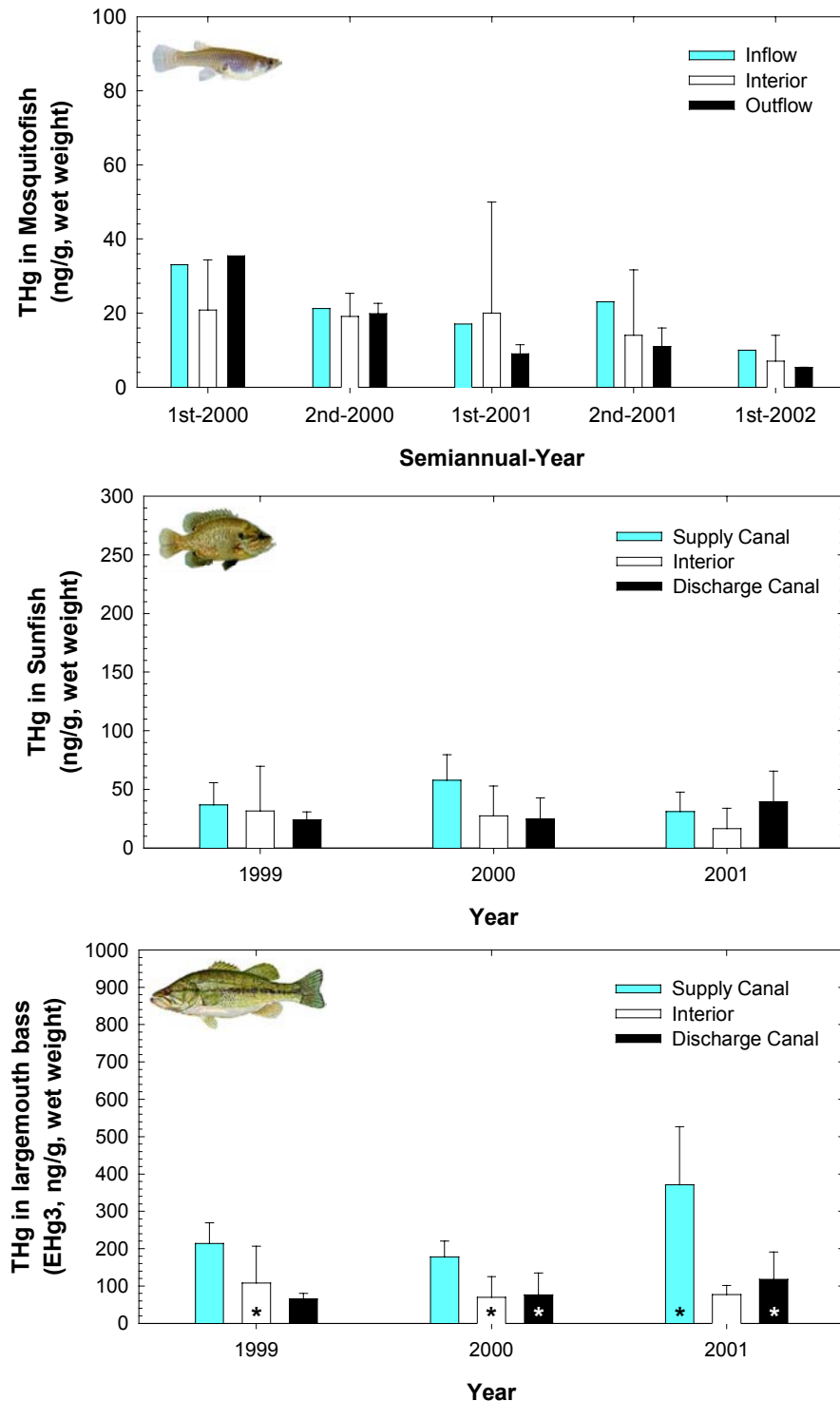


Figure 10. Mercury concentrations in (a) mosquitofish composites, (b) whole sunfish, and (c) fillets of largemouth bass collected at STA-1W. Note: the latter are reported as the expected concentration in a three-year-old fish, EHg3, unless this could not be calculated (*, for details, see Table 5), in which case, the arithmetic mean is reported

As with surface water, mosquitofish also consistently exhibited a negative percent change in tissue Hg across STA-1W, with fish collected at the outflow containing about 50 percent less mercury than that of fish collected at the inflow (**Table 4**). As discussed below, this pattern, which was unparalleled in the other STAs, was also observed in sunfish and largemouth bass.

As is evident from **Table 5** and **Figure 10**, sunfish continued to have mercury levels much lower than those observed in sunfish at the other STAs and locations within the Everglades (**Appendix 4B-3**). Further, this pattern does not appear to be changing, i.e., there are no obvious temporal increases (**Figure 10**). Nevertheless, similar to the other STAs, spatial patterns in tissue Hg were observed in 2001. However, locational differences in size (i.e., total length) of sunfish from STA-1W were also significant (ANOVA; $df = 5, 99$; $f = 10.2$; $p < 0.001$). While the relationship between size and tissue Hg is relatively weak at STA-1W compared to other sites, it may have confounded interpretation of tissue Hg concentrations. Sunfish exhibited a slight positive percent change in tissue Hg across the STA in 2001; however, cumulative mean Hg concentration remains lower in fish from the discharge canals (**Table 5**).

Similar to sunfish, largemouth bass from STA-1W contained much lower concentrations of Hg than did bass from the other STAs (**Table 6** and **Figure 10**). Moreover, Hg levels in bass from STA-1W were also much lower than concentrations observed in fish from downstream sites in the WCAs (**Appendix 4B-3**). As mentioned previously, as with mosquitofish and sunfish, Hg in bass exhibited a negative percent change across STA-1W, that is, it declined from the supply canal to discharge canals (–68 percent based on non-standardized concentrations). The difference in tissue Hg between fish caught in 2001 from the supply and discharge canals was significant ($df = 43$, $t = 7.14$, $p < 0.001$), with lower concentrations in bass from the discharge canal. Further, the most obvious temporal trend evident from **Figure 10** is the increase in tissue Hg in supply canal fish. Finally, the mercury burden in EHg3 bass from the interior marshes of STA-1W (77 ± 24 ng/g) was remarkably low when compared to other bass in South Florida.

In terms of the risk to fish-eating wildlife, fish from STA-1W continue to have tissue-Hg levels well below both the USEPA and USFWS guidance level for predator protection. Thus, unlike most Everglades areas, fish-eating wildlife feeding at STA-1W do not appear to be at any risk from Hg exposure.

STA-2

As stated previously, STA-2 cells 2 and 3 met mercury startup criteria on September 26, 2000, and November 9, 2000, respectively. Cell 1 still has not met startup criteria as of this writing. Refer to **Appendix 4B-3** for a detailed discussion of the results of expanded mercury monitoring of STA-2 in accordance with permit No. 0126704 modified on August 9, 2001.

Key findings from that monitoring are as follows:

1. There were no violations of the Florida Class III numerical Water Quality Standard (WQS) of 12 ng total mercury (THg)/L at the outflow of STA-2 (i.e., G-335); however, outflow from cell 1 reached 12 ng/L during drawdown of the cell. As such, the project has met the requirements of Section 6.i of the Mercury Monitoring Program of the referenced permits.
2. Results from the expanded monitoring of mercury in surface water and fish tissues strongly indicated that anomalous methylmercury production was restricted to cell 1.

3. A positive gradient was observed in MeHg levels in surface water and fish tissues from the inflow in the north to the outflow in the southern portion of cell 1 and, consequently, site C1A was found not to be representative of conditions within STA-2 cell 1.
4. Further, due to the configuration and design of cell outlets, a single grab sample upstream of the outflow pump at G-335 was found to be unrepresentative of discharge under steady state flow.
5. The dramatic fluctuations and concentrations of THg and MeHg in the discharge canal decreased following drawdown and reduction in discharge from cell 1.
6. A gradient in cell 1 stage may have resulted in relatively shallow depths in the southern portion of the cell, and in turn this might have had an effect on sediment biogeochemistry, particularly redox and mercury methylation.
7. Hg levels in STA-2 fish exhibited spatial patterns consistent with patterns observed in surface water concentrations.
8. Average Hg concentrations in sunfish caught in a swale within cell 1 in April 2002, which was otherwise dry, were twice the basin-wide mean concentration for sunfish.
9. Levels of mercury in largemouth bass were also elevated relative to other STAs and downstream sites, with the expected mean concentration in a three-year-old fish from the discharge canal being 1,148 ng/g.
10. While the area of contact and exposure potential were lowered substantially by draining cell 1, fish-eating wildlife remained at some risk of adverse chronic effects from mercury exposure if feeding preferentially at STA-2 in the shallow pools that remained.

LITERATURE CITED

- Bloom, N.S. 1992. On the chemical form of mercury in edible fish and marine invertebrates. *Can. J. Fish. Aquat. Sci.*, 49: 1010-1017.
- Delfino, J.J., T.L. Crisman, J.F. Gottgens, B.R. Rood, and C.D.A. Earle. 1993. Spatial and temporal distribution of mercury in Everglades and Okefenokee wetland sediments. Final Project Report (April 1, 1991 through June 30, 1993) to South Florida Water Management District (contract no. C91-2237), USGS (contract no. 14-08-0001-G-2012) and Florida DER (contract no. WM415).
- Fink, L., D.G. Rumbold, and P. Rawlik. 2000. ENR Project mercury studies: 1994-1999. Appendix 7.5 In *2000 Everglades Consolidated Report*. South Florida Water Management District, West Palm Beach, FL.
- Fink, L., D.G. Rumbold, and P. Rawlik (1999). The Everglades mercury problem. Chapter 7 in *Everglades Interim Report*. Report to the Florida Legislature. South Florida Water Management District, West Palm Beach, FL.
- Florida Governor's Mercury in Fish and Wildlife Task Force. 1991. Mercury Technical Committee (MTC) Interim Report.
- Florida Panther Interagency Committee. 1991. Status report, Mercury contamination in Florida Panthers. Technical Subcommittee of the Florida Panther Interagency Committee Florida Game and Fresh Water Fish Commission, U.S. Fish and Wildlife Service, and Everglades National Park.
- FTN Associates. 1999. Everglades mercury baseline report for the Everglades Construction Project under permit No. 199404532. Prepared for the South Florida Water Management District. West Palm Beach, FL.
- Gilbert, R.O. 1987. Statistical Methods for Environmental Pollution Monitoring. Van Nostrand Reinhold. New York.
- Grieb, T.M., Driscoll, C.T., Gloss, S.P., Schofield, C.L. Bowie, G.L. and Porcella, D.B. 1990. Factors affecting mercury accumulation in fish in the upper Michigan peninsula. *Environ. Toxicol. Chem.*, 9: 919-930.
- Hakanson, L. 1980. The quantification impact of pH, bioproduction and Hg-contamination on the Hg content of fish (pike). *Environ. Pollut. (Series B)*, 1: 285-304.
- Heaton-Jones, T.G., B.L. Homer, D.L. Heaton-Jones, and S.F. Sundlof. 1997. Mercury distribution in American alligators (*Alligator mississippiensis*) in Florida. *J. Zoo and Wildlife Medicine*, 28: 62-70.
- Hurley, J.P., D.P. Krabbenhoft, L.B. Cleckner, M.L. Olson, G.R. Aiken, and P.S. Rawlik, Jr. 1998. System controls on the aqueous distribution of mercury in the northern Florida Everglades. *Biogeochemistry*, 40: 293-311.
- Jagoe, C.H., B. Arnold-Hill, G.M. Yanochko, P.V. Winger, and I.L. Brisbin Jr. 1998. Mercury in alligators (*Alligator mississippiensis*) in the southeastern United States. *Sci. Total Environ.*, 213: 255-262.

- Krabbenhoft, D.P., and L.E. Fink. 2001. The effect of drydown and natural fires on mercury methylation in the Florida Everglades. Appendix 7-8 in *2001 Everglades Consolidated Report*. South Florida Water Management District, West Palm Beach, FL.
- Krabbenhoft, D.P., J.P. Hurley, M.L. Olson, and L.B. Cleckner. 1998. Diel variability of mercury phase and species distributions in the Florida Everglades. *Biogeochemistry*, 40: 311-325.
- Lange, T.R., D.A. Richard, and H.E. Royals. 1998. Trophic Relationships of Mercury Bioaccumulation in Fish from the Florida Everglades. Annual report. Florida Game and Fresh Water Fish Commission, Fisheries Research Laboratory, Eustis, FL. Prepared for the Florida Department of Environmental Protection, Tallahassee, FL. August.
- Lange, T.R., D.A. Richard, and H.E. Royals. 1999. Trophic relationships of mercury bioaccumulation in fish from the Florida Everglades. Annual report. Florida Game and Fresh Water Fish Commission, Fisheries Research Laboratory, Eustis, FL. Prepared for the Florida Department of Environmental Protection, Tallahassee, FL. April.
- Lange, T.R., D.A. Richard and H.E. Royals. 2000. Long-term trends of mercury bioaccumulation in Florida's largemouth bass. Abstract from the Annual All-Investigators' Meeting: South Florida Mercury Science Program, May 9 through 11, 2000. Palm Harbor, FL.
- Loftus, W.F., J.C. Trexler, and R.D. Jones. 1998. Mercury transfer through the Everglades aquatic food web. Final report to the Florida Department of Environmental Protection. Tallahassee, FL. December 1998.
- Pollman, C.D., and T.D. Atkeson. 2000. Long-term trends in mercury atmospheric inputs and deposition in South Florida. Abstract from the Annual All-Investigators' Meeting: South Florida Mercury Science Program, May 9 through 11, 2000. Palm Harbor, FL.
- Rawlik, P. 2001. Mercury concentrations in mosquitofish from treatment wetlands in the northern Everglades. Appendix 7-15 in *2001 Everglades Consolidated Report*. South Florida Water Management District, West Palm Beach, FL.
- Roelke, M.E., and C.M. Glass. 1992. Florida Panther Biomedical Investigation. Annual Performance Report on Statewide Wildlife Research: July 1, 1991 through June 30, 1992. Study E-1-II-E-6. Florida Game and Fresh water Fish Commission, Tallahassee, FL.
- Rumbold, D.G. 2000. Methylmercury risk to Everglades wading birds: a probabilistic ecological risk assessment. Appendix 7.3b In *2000 Everglades Consolidated Report*. South Florida Water Management District, West Palm Beach, FL.
- Rumbold, D.G., and P. Rawlik. 2000. Annual permit compliance monitoring report for mercury in stormwater treatment areas and downstream receiving waters. Appendix 7-2 in *2000 Everglades Consolidated Report*. South Florida Water Management District, West Palm Beach, FL. January.
- Rumbold, D.G., L. Fink, K. Laine, F. Matson, S. Niemczyk, and P. Rawlik (2001a). Annual permit compliance monitoring report for mercury in stormwater treatment areas and downstream receiving waters of the Everglades Protection Area. Appendix 7-9 in *2001 Everglades Consolidated Report*. South Florida Water Management District, West Palm Beach, FL.

- Rumbold, D.G., L. Fink, K. Laine, F. Matson, S. Niemczyk, and P. Rawlik (2001b). Stormwater Treatment Area 6 Followup Mercury Studies. Appendix 7-13 in *2001 Everglades Consolidated Report*. South Florida Water Management District, West Palm Beach, FL.
- SFWMD. 1997a. Operation plan: Stormwater Treatment Area No. 6, Section 1. South Florida Water Management District, West Palm Beach, FL.
- SFWMD. 1997b. Everglades Nutrient Removal Project: 1996 Monitoring Report. South Florida Water Management. Prepared for the Florida Department of Environmental Protection, Tallahassee, FL.
- SFWMD. 1998a. Operation Plan: Stormwater Treatment Area 5. Draft. South Florida Water Management District, West Palm Beach, FL.
- SFWMD. 1998b. Operation Plan: Stormwater Treatment Area 1 West. Draft. South Florida Water Management District, West Palm Beach, FL.
- SFWMD. 1998c. Annual permit compliance monitoring report for mercury in stormwater treatment areas and downstream receiving waters. South Florida Water Management District, Prepared for the Florida Department of Environmental Protection, Tallahassee, FL.
- SFWMD. 1999a. Operation Plan: Stormwater Treatment Area 2. Revision 1.0. South Florida Water Management District, West Palm Beach, FL.
- SFWMD. 1999b. Everglades Nutrient Removal Project: 1998 Monitoring Report. South Florida Water Management. Prepared for the Florida Department of Environmental Protection, Tallahassee, FL.
- SFWMD. 1999c. Stormwater Treatment Area 6, Section 1 Annual monitoring report. South Florida Water Management. Prepared for the Florida Department of Environmental Protection, Tallahassee, FL.
- Sundlof, S.F., M.G. Spalding, J.D. Wentworth, and C.K. Steible. 1994. Mercury in the liver of wading birds (Ciconiiformes) in southern Florida. *Arch. Environ. Cont. Toxicol.*, 27: 299-305.
- USEPA. 1998. South Florida Ecosystem Assessment. Volume 1. Final Technical Report. Phase I. Monitoring for adaptive management: implications for ecosystem restoration. Region 4 and Office of Research and Development. Athens, GA. EPA-904-R-98-002.
- Ware, F.J., H. Royals, and T. Lange. 1990. Mercury contamination in Florida largemouth bass. *Proc. Ann. Conf. Southeast Assoc. Fish Wildl. Agencies*. 44: 5-12.
- Watras, C. 1993. Potential impact of the Everglades Nutrient Removal Project on the Everglades mercury problem. (EV 930034). Unpublished report prepared for the South Florida Management District. University of Wisconsin, Madison. October.
- Wren, C.D., and H.R. MacCrimmon. 1986. Comparative bioaccumulation of mercury in two adjacent freshwater ecosystems. *Water Research*, 20: 763-769.
- Zar, J.H. 1996. Biostatistical analysis (3rd edition). Prentice-Hall, NJ.